

# **A New Approach to Characterizing Organic Aerosol (wood smoke and diesel exhaust particulate) Using Subcritical Water Fractionation**

Alena Kubátová

Energy & Environmental Research Center, University of North Dakota, Box 9018  
Grand Forks, ND USA 58202-9018

E-mail: [akubatova@undeerc.org](mailto:akubatova@undeerc.org); Telephone (701) 777 2498, Fax: (701) 777 5181

Mayia Fernandez

Present address: Sofresid Conseil, La Defense3, 4/6 Avenue d'Alsace  
92040 Paris La Defense Cedex, FRANCE

E-mail: [mayia.fernandez@netcourrier.com](mailto:mayia.fernandez@netcourrier.com)

Steven B. Hawthorne

Energy & Environmental Research Center, University of North Dakota, Box 9018  
Grand Forks, ND, USA 58202-9018

E-mail: [shawthorne@undeerc.org](mailto:shawthorne@undeerc.org); Telephone (701) 777 5256, Fax: (701) 777 5181

## **Summary**

The toxic effects on health of fine particulate aerosol (particles smaller than 2.5  $\mu\text{m}$ ) are discussed in a number of studies.<sup>1,2</sup> In contrast to inorganic aerosols, which are often well characterized, only ca. 15%–50% of the organic carbonaceous (OC) particulate mass has been characterized. The characterized compounds are almost exclusively nonpolar.<sup>3</sup> The limited knowledge of OC fractions is due to the use of organic solvents, which are able to extract only nonpolar or slightly polar organics. In addition, polar compounds cannot usually be analyzed via gas chromatography with a mass spectrometer (GC/MS). Consequently, the toxicity of organic aerosols has been primarily studied for nonpolar OC (for example, polyaromatic hydrocarbons [PAHs]), while the toxicity of significant polar fractions of OC is not known. Moreover, with conventional solvent extracts, toxicity tests on OC are difficult to perform because the solvents employed are toxic for biological systems. Finally, polar organics may also be important for mobilizing toxic metals from air particulates in biological systems by chelation reactions.<sup>4</sup>

Recently, subcritical water (defined as hot water under sufficient pressure to maintain the liquid state) has been used to extract organics with a wide range of polarities. The advantage of water extraction is not only in the “nontoxicity” of water, but also in the ability of water to change polarity by changing the temperature. At lower temperatures (e.g., 25°C to 100°C), water can extract polar compounds; with increasing temperature (e.g., to 250°C), the polarity of water decreases and becomes comparable to the polarity of organic solvents, allowing nonpolar compounds to be extracted.<sup>5</sup> Earlier studies have shown that compounds of different polarities such as phenols, PAHs, and alkanes could be sequentially extracted from a petroleum waste sludge by increasing subcritical water temperature.<sup>6</sup> A particular

advantage of subcritical water extraction is that the resultant extracts can be used directly for toxicity tests and, thus, can be used to determine the importance of individual water fractions for further characterization.

In this study, subcritical water was used for the first time for the extraction and fractionation of organic atmospheric particulate. Two different types of carbonaceous aerosol, diesel exhaust particulate (a relatively nonpolar matrix) and wood smoke particulate (a polar matrix), were sequentially extracted using subcritical water at temperatures ranging from 25°C to 300°C.

To evaluate the importance of each fraction, a toxicity test was performed with Polytox, a rapid test for measuring the toxicity of wastewater based on the inhibitory effect on respiration rate of mixed bacterial cultures. For both aerosols tested, the fractions extracted at lower temperatures (higher-polarity organics) exhibited the highest toxicity. The toxicity of diesel exhaust particulate also increased for the higher-temperature fraction collected at 300°C. The diesel exhaust fractions collected at 100°C, 150°C, and 200°C also showed at least 10% inhibition of bacterial respiration, but results were not unequivocal because the samples themselves had a tendency to consume oxygen.

The initial mass balance data showed that, while traditionally used organic solvents such as acetone or methylene chloride extracted ca. 30% of wood smoke and diesel exhaust particulate, the total mass recovered with subcritical water was ca. 60%. In contrast to the total mass balance, the extractable and elutable mass obtained from gas chromatography with flame ionization detection (GC/FID) was comparable for organic solvents and subcritical water. Although quantitative analysis based on GC did not bring additional information, the identification of individual components in each fraction of wood smoke particulate using GC/MS showed trends that can be related to the toxicity observed. The lower-temperature fractions of wood smoke particulate, collected at 25° and 50°C, contained a higher concentration of phenolic compounds, lignin pyrolysis products such as syringol and levoglucosan derivatives, phenols, and benzenediols. Interestingly, a high quantity of levoglucosan, a typical marker of wood burning, was found in water extracts while not observed in acetone extracts. Unfortunately, GC/MS analysis of diesel exhaust was not as informative as that of wood smoke particulate, because the GC elutable fraction of diesel exhaust consists mainly of alkanes, which are not extractable by water.

Further characterization of individual water fractions was based on elemental CHN analysis, determination of sulfur content, pH determination, and inductively coupled plasma mass spectrometry (ICP/MS) metal analysis. For lower-temperature fractions (which were the most toxic), increased sulfur content was also observed. The initial concentration of sulfur in diesel exhaust particulate was 40 mg/g. In the first fraction collected at 25°C, 50% of the sulfur was found, and an additional 25% was recovered in the 50°C fraction. The analyses of diesel exhaust particulate for metals revealed a similar trend of increased concentration of some metals in the most polar fraction. The fraction collected at 25°C contained 75% of total zinc, which was the most abundant metal present at a concentration of 1.8 mg/g. The concentration of all other metals (Mn, Cr, Cu, Ba, Pb) in diesel exhaust particulate was in the range of 20–70 µg/g, and only manganese showed extraction behavior similar to zinc.

In future work, further attention will be given to additional toxicity tests to confirm current results. As in this work, the main effort will be to focus on the characterization of the most toxic fractions.

## References

1. M.P. Hannigan, G.R. Cass, B.W. Penman, C.L. Crespi, A.L. Lafleur, W.F. Busby Jr. and W.G. Thilly, *Environ. Sci. Technol.*, 31, 438 (1997).
2. T. Reichhardt, *Environ. Sci. Technol.*, 30, 68A (1996).
3. C.C. Christoforou, L.G. Salmon, M.P. Hannigan, G.R. Cass, *Air & Waste Manage. Assoc.*, 50, 43 (2000).
4. Steve Benson, EERC (personal communication, October, 2000).
5. S.B. Hawthorne, D.J. Miller and A.J.M. Lagadec, Patent 6 001 256, 2000.
6. Y. Yang, S.B. Hawthorne and D.J. Miller, *Environ. Sci. Technol.*, 31, 430 (1997).

## Acknowledgement

This work was sponsored by the United States Department of Energy under Contract FC26-98FT40320.